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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C03C 13/06

A1

(11) International Publication Number: WO 96/30314

(43) International Publication Date: 3 October 1996 (03.10.96)

(21) International Application Number: PCT/EP96/01181

(22) International Filing Date: 19 March 1996 (19.03.96)

(30) Priority Data:
195 12 145.7 31 March 1995 (31.03.95) DE

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(81) Designated States: AU, BR, CA, CN, CZ, FI, HU, IS, JP, KR, NO, NZ, PL, SI, SK, TR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: A MINERAL FIBER COMPOSITION

(57) Abstract

A biodegradable mineral fiber composition, characterized by the following constituents in percent by weight: SiO_2 45 to 60; Al_2O_3 0 to 3; CaO 20 to 40; MgO 3 to 15; Na_2O 0 to 2; K_2O 1 to 10; $Na_2O + K_2O$ 1 to 12; TiO_2 0 to 3; Fe_2O_3 0 to 3; others 0 to 5.

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A mineral fiber composition

This invention relates to a mineral fiber composition which is biodegradable.

The prior art describes some mineral fiber compositions which are said to be biodegradable.

Biodegradability of mineral fiber compositions is of great importance since various studies indicate that mineral fibers with very small diameters in the range of less than 3 microns are suspected to be carcinogenic, while biodegradable mineral fibers with such dimensions show no carcinogenicity.

However, mineral fiber compositions must also have good workability by known methods for producing mineral wool with a small diameter, in particular the jet process. This involves in particular a sufficient processing range of for example 80°C and suitable viscosity of the glass melt.

The mechanical and thermal properties of mineral fibers, or the products made therefrom, are also of crucial importance. Mineral fibers are used for example for insulating purposes to a great extent. Sufficient temperature resistance of the mineral fibers is necessary in particular for use in the industrial sector.

The problem of the invention is to provide a novel mineral fiber composition which is distinguished by biodegradability, has good temperature resistance and can be processed well.

The invention is based on the finding that this problem can be solved by a mineral fiber composition which consists substantially of silicon dioxide and alkaline-earth oxides, and further contains substantially potassium oxide as a melting accelerator and a considerable proportion of aluminum ox-

ide for increasing temperature resistance.

It has turned out that such mineral fiber compositions fulfill the combination of necessary properties, namely biodegradability, sufficient temperature resistance for insulation objects in industry, as well as good workability in the production of the mineral wool as such and the products. This simultaneously means that the upper devitrification temperature of the melt is preferably under 1320°C. The mean fiber diameter is preferably 3 microns or less.

The inventive glass fiber compositions have considerable amounts of potassium oxide but only small amounts of sodium oxide. The presence of potassium oxide produces a clear increase in glass viscosity and improves temperature resistance by around 40 to 50°C as compared to sodium-containing glass.

The subject of the invention is a mineral fiber composition which is biodegradable, characterized by the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	0 to 3
CaO	20 to 40
MgO	3 to 15
Na_2O	0 to 2
K_2O	1 to 10
$Na_2O + K_2O$	1 to 12
TiO_2	0 to 3
Fe_2O_3	0 to 3
Others	0 to 5.

The inventive mineral fiber compositions are readily drawable in particular by the jet process, i.e. one obtains a

fine, low-shot mineral wool.

The mineral wool reaches a high temperature resistance of at least 740°C and shows good biodegradability.

The inventive mineral fiber compositions can preferably be melted in melting chambers fueled with fossile fuels, in particular natural gas, at melting temperatures from 1350 to 1450°C. Such melting chambers can produce a homogeneous melt, which is a prerequisite for constant product quality. Homogeneity of the glass melt also facilitates the reproducibility of the fiberizing process and thus of the thermal and mechanical product properties. Furthermore, the constant chemical composition of the thus produced mineral wool leads to controllable biodegradability.

In particular the addition of aluminum oxide increases the temperature resistance of the mineral wool.

The inventive mineral fiber compositions preferably have the following constituents in percent by weight:

SiO_2	50 to 58
Al_2O_3	0.2 to 2.5
CaO	25 to 35
MgO	5 to 10
Na_2O	< 1
K_2O	2 to 8
$Na_2O + K_2O$	2 to 8
TiO_2	0 to 1
Fe_2O_3	0 to 1
Others	0 to 5.

Mineral fiber compositions are especially preferred with the following constituents in percent by weight:

SiO_2	52 to 57
Al_2O_3	< 2
CaO	28 to 34
MgO	6 to 9
Na_2O	< 1
K_2O	2 to 6
$Na_2O + K_2O$	2 to 6
TiO_2	0 to 1
Fe_2O_3	0 to 1
Others	0 to 5.

For assessment of biodegradability the standard powder test of the Deutsche Glasgesellschaft was used. This is an easily performed method and gives a sufficient measure of biodegradability. The method is described in L. Springer, "Laboratoriumsbuch für die Glasindustrie", 3rd ed. 1950, Halle/S, W. Knapp Verlag.

The thermal behavior of the mineral fibers was determined by the so-called "Swedish method". This method uses a silit pipe furnace with a horizontal working pipe open on both sides with a length of 350 mm and an inside diameter of 27 mm. In the center of the furnace there is a ceramic supporting plate with dimensions of 30 x 20 x 3 mm for positioning the test sample. The test sample has dimensions of 12 x 12 x 12 mm or 12 mm Ø x 12 mm height. The gross density is normally 100 kg/m³. The temperature increase is 5 K/min. The change in test sample height is determined continuously with a reading optic.

The invention will be described more closely in the following using examples.

Example 1

A mineral wool was produced with the following composition in percent by weight:

SiO_2	55.6
Al_2O_3	0.4
Fe_2O_3	0.5
CaO	30.5
MgO	7.0
Na_2O	0.2
K_2O	5.6.

This composition could be readily fiberized by the jet process at a drawing temperature between 1340 and 1400°C into mineral fibers with a mean diameter of 2.0 to 10 microns.

An investigation by the standard powder test of the Deutsche Glasgesellschaft yielded a value of 40 mg/kg and thus a value for high biodegradability.

Determination of thermal behavior by the "Swedish method" yielded a temperature resistance of 740°C with 5% height reduction.

Example 2

A mineral wool was produced with the following composition in percent by weight:

SiO_2	53.4
Al_2O_3	2.0
Fe_2O_3	0.3
CaO	32.4
MgO	8.2
Na_2O	0.4
K_2O	2.6.

This composition could be readily processed by the jet process at a drawing temperature between 1340 and 1400°C into mineral fibers with a mean diameter of 2.0 to 10 microns.

An investigation by the standard powder test of the Deutsche Glasgesellschaft yielded a value of 48 mg/kg and thus a value for high biodegradability.

Determination of thermal behavior by the "Swedish method" yielded a temperature resistance of 750°C with 5% height reduction.

Claims

1. A mineral fiber composition which is biodegradable, characterized by the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	0 to 3
CaO	20 to 40
MgO	3 to 15
Na_2O	0 to 2
K_2O	1 to 10
$Na_2O + K_2O$	1 to 12
TiO_2	0 to 3
Fe_2O_3	0 to 3
Others	0 to 5.

2. The mineral fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	50 to 58
Al_2O_3	0.2 to 2.5
CaO	25 to 35
MgO	5 to 10
Na_2O	< 1
K_2O	2 to 8
$Na_2O + K_2O$	2 to 8
TiO_2	0 to 1

Fe_2O_3	0 to 1
Others	0 to 5.

3. The mineral fiber composition of claim 1 or 2, characterized by the following constituents in percent by weight:

SiO_2	52 to 57
Al_2O_3	< 2
CaO	28 to 34
MgO	6 to 9
Na_2O	< 1
K_2O	2 to 6
$Na_2O + K_2O$	2 to 6
TiO_2	0 to 1
Fe_2O_3	0 to 1
Others	0 to 1.

INTERN. /ONAL SEARCH REPORT

International Application No
PCT/EP 96/01181

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE,A,44 27 368 (GRUENZWEIG & HARTMANN) 8 February 1996 see the whole document	1-3
X	FR,A,2 690 438 (SAINT GOBAIN ISOVER) 29 October 1993 see page 9	1-3
X	WO,A,92 09536 (PAROC OY AB) 11 June 1992 see the whole document	1-3
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☐ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 June 1996	- 1. 07. 96

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNA NAL SEARCH REPORT

Int. ional Application No
PCT/EP 96/01181

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-4427368	08-02-96	AU-B-	2885895	04-03-96
		CA-A-	2171447	15-02-96
		WO-A-	9604213	15-02-96
		FI-A-	961471	01-04-96
		NO-A-	961335	01-04-96
FR-A-2690438	29-10-93	AU-B-	4263293	29-11-93
		BR-A-	9305492	11-10-94
		CA-A-	2110998	11-11-93
		CN-A-	1078708	24-11-93
		CZ-A-	9302865	19-10-94
		EP-A-	0596088	11-05-94
		WO-A-	9322251	11-11-93
		HU-A-	67212	28-03-95
		JP-T-	6508600	29-09-94
		NO-A-	934725	20-12-93
		SI-A-	9300218	31-12-93
		SK-A-	146893	09-11-94
		ZA-A-	9302874	01-06-94
WO-A-9209536	11-06-92	FI-B-	93346	15-12-94
		AT-T-	117662	15-02-95
		AU-B-	8908791	25-06-92
		DE-D-	69107091	09-03-95
		DE-T-	69107091	17-08-95
		EP-A-	0558548	08-09-93
EP-A-0459897	04-12-91	FR-A-	2662688	06-12-91
		AT-T-	121378	15-05-95
		AU-B-	642493	21-10-93
		AU-B-	7731891	05-12-91
		CA-A-	2043699	02-12-91
		CN-A-	1059135	04-03-92
		DE-D-	69108981	24-05-95
		DE-T-	69108981	07-12-95
		ES-T-	2073136	01-08-95
		HU-B-	212280	29-04-96
		JP-A-	4228455	18-08-92
		PL-B-	167825	30-11-95
		US-A-	5250488	05-10-93